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$Cu(In,Ga)(Se,S)_2$ Solar Cell Research in Solar Frontier K.K. with 22.3% World-Record Efficiency

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Abstract

Record efficiency of 22.3% has been achieved for $Cu(In,Ga)(Se,S)_2$ solar cell. Compared to our previous champion cell with 20.9% efficiency, the major breakthrough is due to the increased open-circuit voltage (V_{OC}), benefited from the post-deposition treatment using potassium (K) source. Further characterizations (CV, V_{OC}-T, Suns-V_{OC}) indicate that the recombination rates at the interface and depletion region were reduced significantly. This is supported by the EBIC images which show a prolonged carrier collection length away from the p-n interface. Based on the results, device simulation suggests that further reduction of surface defect density could enhance the V_{OC} towards 760 mV.

1. Introduction

$Cu(In,Ga)Se_2$ solar cells have shown consistent efficiency improvement beyond 20% in recent years, with major contribution from post-deposition alkali treatment after the formation of the thin film absorber [1]. Intentional K doping, together with the unintentional Na diffusion from the glass substrate; have consistently shown an improved V_{OC} and FF by several laboratories [1-2]. In Solar Frontier, we have also attempted post K-treatment on our $Cu(In,Ga)(Se,S)_2$ thin film. As a result, the world record efficiency for ZnO/CdS/CIGS solar cell was renewed, giving 22.3% efficiency. A general V_{OC} enhancement of ~30 mV was usually observed for the samples with post K-deposition and annealing. FF was also improved as a result of the higher V_{OC}. By replacing ZnO with optimized (Zn,Mg)O, Cd-free (Zn,Mg)O/Zn(O,S,OH)/CIGS solar cell has achieved efficiency of 22.0%.

To understand the mechanism of V_{OC} enhancement, various characterizations have been performed on the sister cell (Cell 1') of the current 22.3% champion cell with K-treatment. Temperature dependent V_{OC} measurement (V_{OC}-T) was done to extract the activation energy (E_a), which shed light on the recombination mechanism. The minimum band gap (E_g) was extracted from the peak of the first order derivative ($d(QE)/d\lambda$) of the IQE curve. Furthermore, capacitance-voltage (CV) measurement was performed to obtain the carrier density and the built-in potential (V_{bi}). Together with Suns-V_{OC} measurement, the recombination rates at each region (interface, depletion and bulk) of the solar cell can be derived [3]. Comparing with our previous 20.9% champion (Cell 2, without K-treatment), the V_{OC} improvement mechanism can be further revealed.

2. Results and Discussion

Fig. 1 shows the J-V curves of Cell 1 & 2. Both of the J-V curves are measured and certified by Fraunhofer ISE and re-plotted here for comparison. The J-V curves are fitted by one-diode model employing Lambert-W function to extract the device parameters, as shown in Table I. Although E_g is higher for the current champion, it does not fully account the V_{OC} increment of 36.1 mV as the V_{OC} deficit ($V_{OC},def = Eg/q - V_{OC}$) normally increases with higher E_g due to deeper defect states related to higher S- [4] or Ga-content [5]. In Cell 1 with higher E_g, V_{OC},def was maintained, possibly due to the passivation of surface defect by post K-treatment after the formation of $Cu(In,Ga)(Se,S)_2$ absorber, as explained later.

TABLE I. Extracted device parameters by fitting the LJV curves using Lambert-W function. R_{SL} is the series resistance, R_{PL} is the shunt resistance, n_L is the ideality factor, and J_0 is the reverse saturation current density.

Cell	Eff (%)	E_g (eV)	V_{OC},def (mV)	R_{SL} ($\Omega.cm^2$)	R_{PL} ($\Omega.cm^2$)	n_L	J_0 (A/cm^2)
1	22.3	1.11	388.1	0.20	1312	1.45	1.64E-10
2	20.9	1.07	384.2	0.28	580	1.42	2.95E-10

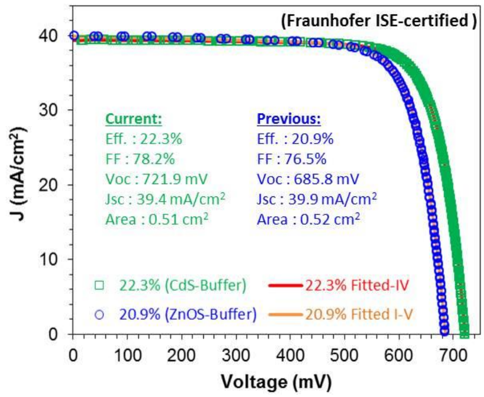

Fig. 1 LJV curves for the current 22.3% and previous 20.9% champion CIGS solar cells. The device parameters are listed inside the figure, and the fitted parameters are listed in Table I above.

From V_{OC}-T measurement, E_a of Cell 1' (Cell 2 [6]) was found to be 1.18 (1.05) eV, larger (smaller) than the extracted E_g as shown in Table 1. With E_a much larger than E_g

in Cell 1', this suggests that the recombination at the interface and depletion region is reduced compared to Cell 2 [7]. From CV measurements, the acceptor concentrations (N_A) for Cell 1' and Cell 2 are 2.7×10^{16} and $2.2\times10^{16}cm^{-3}$, respectively, while the V_{bi} are 0.80V for Cell 1' and 0.77V for Cell 2 [6]. Together with Suns-V_{OC} measurement, recombination coefficients at various regions can be calculated [3]. The respective recombination rates for Cell 1' & 2 are tabulated in Table II above. For both cells, bulk recombination is higher than the interface and depletion recombination. However, the recombination rates at the interface and depletion region of Cell 1 were significantly reduced compared to Cell 2. Note that the recombination coefficients are calculated based on the mean-E_g of the respective absorbers, which explains the different values obtained from the previous report [6]. Lastly, the reduced recombination velocity at the surfaces were well reflected in the EBIC images of Cell 1, which shows a prolonged carrier collection length away from the p-n interface.

TABLE II. Recombination coefficient (independent of voltage) and recombination rates at the interface (R_i), depletion region (R_d), and the bulk (R_b) at $V = V_{OC}$.

Cell	R_{i0}	R_{d0} ($cm^{-2}s^{-1}$)	R_{b0}	R_i	R_d ($\times10^{16}$ $(cm^{-2}s^{-1})$)	R_b
1'	9.2×10^4	4.5×10^{10}	2.5×10^5	8.7	4.4	23.6
2	4.1×10^5	1.7×10^{11}	4.3×10^5	13.6	10.0	14.3

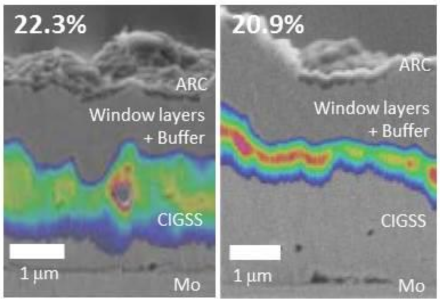

Fig. 2 EBIC images of the current 22.3% champion CIGS solar cell and our previous 20.9% cell, illustrating a longer carrier collection length from the p-n junction.

Reduced recombination rates at the interface and depletion region suggests reduced defects in this region, possibly resulted from post K-treatment. Device simulation was performed with SCAPS, with defect level of 0.92eV above the valence band maximum, electron and hole capture cross sections of 3.29×10^{-13} and 2.22×10^{-13} cm^{-2}, respectively (measured from deep-level transient spectroscopy). Fig. 3 shows the simulated J-V curves with varying defect density (N_t) at the right side of the CIGS layer (logarithmic decay from the left side). The J-V behaviour of Cell 1 was regenerated with N_t=$1.9\times10^{10}cm^{-3}$ and verified by simulating JV-T and Suns-V_{OC} using the same model (which matches very closely with the experimental results). Finally, the simulation also suggests that further reducing N_t to $1\times10^7cm^{-3}$ (almost negligible) will result in V_{OC} approaching 760mV (Eff=23.8%).

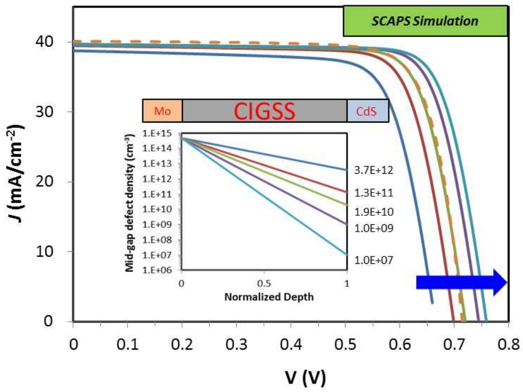

Fig. 3 SCAPS device simulation with different defect profiles as shown in the inset. Simulated J-V with right-side defect density (inside the CIGS layer) of $1.9E\times10^{10}cm^{-3}$ matches the experimental J-V of the current 22.3% champion cell (dash line).

3. Conclusions

Record efficiency of 22.3% has been achieved in CIGS solar cell, mainly due to the enhanced V_{OC} by post K-treatment. Various electrical characterizations suggest that the recombination velocities at the interface and depletion region were largely reduced. This is further supported by the prolonged carrier collection length in the EBIC images. The origin could be due to a decreased defect density at the interface and depletion region, as suggested from the device simulation. Further improvement beyond 24% efficiency will also require enhancement on the other parameters, such as the inferior ideality factor and shunt resistance to improve the fill factor.

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